

The Reaction of Boric Acid with Wood in a Polystyrene Matrix

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SYNOPSIS

The reaction of boric acid with wood fibers in a polymer melt was examined using ¹³C-nuclear magnetic resonance (NMR), ¹¹B-NMR, differential scanning calorimetry, dynamic mechanical analysis, and component extraction and by the determination of material properties. Samples were blended at 350 and 380°F in a roll mill. The use of a plasticizer in the melt to facilitate the reaction of the acid with the wood fiber was studied. NMR data showed that no significant reaction occurred between the boric acid and the polystyrene. Experimental evidence supports the reaction of boric acid with wood components. The ultimate strength of the composites was either reduced or not significantly altered by the reaction, depending upon conditions. However, the stiffness increased significantly with boric acid additions for the 350°F reactions, but behaved differently for the same additions at 380°F. The glass transition temperature of the polystyrene was lowered by the addition of plasticizer, as expected, while boric acid addition had little effect. Extracted samples showed that some boric acid remained with the wood fraction. These preliminary data suggest that boric acid does react with wood fiber under the conditions of this study. These investigations illustrate the feasibility of performing chemical reactions on the wood phase of wood/polymer composites during the extrusion process. Further research is recommended. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The use of wood as a reinforcing filler in thermoplastics continues to receive much attention from the research community. This attention is justified by the theoretical potential of wood fiber as a reinforcing filler and the gap between theory and reality. The dominant theory guiding current research is that composite performance can be improved by improving the interfacial shear strength between the thermoplastic matrix and the wood fiber by creating chemical bonds across the interface between the two. Also recognized as important in the process of developing useful composites from these materials is

an effective means, either chemical or mechanical, of dispersing the fibers in the matrix.¹

Various compatibilization systems have been developed by many labs: academic, government, and industrial. Previous work by one of the authors incorporated boric acid as one component of a compatibilization system. The nature of the wood-boric acid interaction was of interest in elucidating the mechanism of the overall compatibilization. The objective of this study was to investigate the possibility of a reaction between boric acid and wood flour in a polystyrene melt.

This example of reactive extrusion opens up the possibility of analogous, or subsequent, reactions that might be more effective at improving the properties of the final composite. The reaction studied here suggests that it is practical to chemically modify the wood phase during the extrusion of wood-polymer composites.

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Composites formed from polystyrene, wood flour, and boric acid, with and without a plasticizer, were studied utilizing the determination of mechanical properties and NMR. In addition, glass transition temperatures (T_g) were determined using differential scanning calorimetry and dynamic mechanical analysis (DMA).

EXPERIMENTAL

Materials

Polystyrene (PS) was contributed by Dow Chemical Co., Midland, MI, as the product Styron 685D. The melt flow rate was 1.6.

Wood flour from Douglas fir [*Pseudotsuga menziesii* (Mirb.) Franco] ground to 80–100 mesh was contributed by the Menasha Wood Corp., Olympia, WA, as the product T-14. The T-14 was dried *in vacuo* at 60°C overnight and stored over a silica gel desiccant. This filler was analyzed optically and found to have an average length of 0.9 mm with a standard deviation of 0.6 mm. The average aspect ratio was 9 with a standard deviation of 5.

The plasticizer 1-methyl-2-pyrrolidinone was contributed by ISP Technologies as the product *m*-pyrrol. It was used as received. Reagent-grade boric acid was supplied by J. T. Baker Chemical Co., Phillipsburg, NJ.

Sample Preparation

The wood flour was initially dried for 24 h in a vacuum oven at 60°C. The plastic, filler, and additives were blended in a Brabender Plasticorder fitted with a mixing bowl and roller blades set at 30 rpm and temperatures of 350, 380, or 400°F. The PS was added first and blended for 2 min to ensure complete melting. Boric acid (if required) was added and blended for 4 min. The filler was then added and blended for 8 min. Finally, plasticizer was added (if required) and the sample blended for an additional 8 min. The melt was then removed from the Plasticorder, cooled, and stored for grinding.

The blended samples were ground in a Wiley mill to a particle size of approximately 3 mm (0.1 in.). These powders were then compression-molded in a thermostatted Carver laboratory press. The press conditions were 180°C (360°F) and 6.9 MPa (1000 psi) for 10 min. The sample size was approximately 2 × 13 × 55 mm (0.08 × .5 × 2 in.). The compression mold held five samples.

Material Properties

The modulus of elasticity (MOE) was determined in flexure using a three-point bending apparatus in accordance with ASTM Standard D790-86. Five samples were tested for each determination of MOE wherever possible. In some cases, only three samples were used due to material limitations. The same samples and test procedure were used to determine the ultimate strength, which was defined in this case as the modulus of rupture (MOR).

Extraction Procedure

A small sample (about 5 g) was dissolved in refluxing toluene for 24 h. The wood flour was then separated by filtration and dried in a vacuum oven at 60°C for 24 h. The wood flour was then placed in boiling water for 30 min, then filtered. The aqueous solution was tested for boron using X-ray fluorescence spectroscopy with a Milton Roy Spectronic 301. The remaining wood flour was digested using American Wood Preservers Standard A7-93. The resulting solution was analyzed for boron using a Jarrel-Ash inductively coupled argon plasma spectrometer (ICAP 9000).

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties were determined on a Rheometrics, Inc., RSA-II solids analyzer. The samples were tested at 2° intervals over the temperature range from 30–130°C using a three-point bending geometry and a constant frequency of 1 Hz. Typical sample dimensions for this analysis were 2.8 × 12 × 48 mm.

Differential Scanning Calorimetry (DSC)

Selected samples were analyzed with a Perkin-Elmer DSC-7 calorimeter with a System 1020 Controller under a nitrogen environment. The typical sample size was about 25 mg. The analysis regime included an initial scan from 50 to 150°C at 20°/min to remove thermal history effects, then cooled to 50°C and the data collected at 10°/min to 225°C.

NMR

Solid-state ^{13}C - and ^{11}B -NMR spectra were recorded on a Bruker MSL 400P (9.4 T) multinuclear spectrometer at 100.6 and 128.3 Mhz, respectively. The ^1H — ^{13}C cross-polarization magic-angle spinning

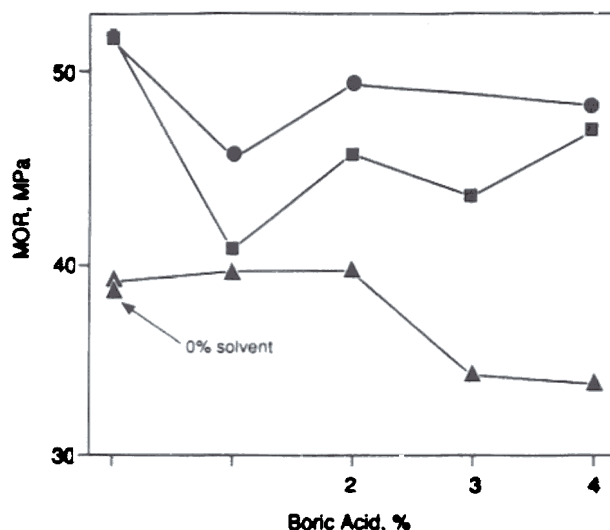


Figure 1 Strength of 65% polystyrene/35% wood flour as a function of boric acid addition for (●) 3% solvent at 350°F, (■) 0% solvent at 350°F, and (▲) 3% solvent at 380°F.

(CP/MAS) NMR spectra were recorded using a contact time of 1.5 ms, a ^1H 90° pulse of 4.5 ms, a recycle delay of 10 s, and spinning rates of 10–15 kHz. Since the 4 mm double-bearing Bruker probe used has a strong and rather broad ^{11}B background which overlaps with the faint signals given by the samples studied here, all the ^{11}B -MAS spectra were recorded with a recycle delay of 2 s and spinning rates of 13–15 kHz, using the following echo pulse sequence: $[\pi/15 - t_1 - \pi/15 - t_2, \text{acquisition}]$, with $t_1 = 60$ ms, and $t_2 = 62$ ms. Preliminary experiments carried out with boric acid showed that this pulse sequence introduces only a small line-shape distortion in the second-order quadrupole powder pattern. ^{11}B is a quadrupolar nucleus with spin $I = \frac{3}{2}$. The quadrupolar interaction is a tensor interaction which may be defined by two parameters, $eq = V_{zz}$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{xx} , V_{yy} , V_{zz} are the principal elements of a tensor describing the electric field gradient (EFG). For a polycrystalline sample, MAS yields an NMR spectrum which is a powder pattern with a characteristic shape determined by the quadrupole coupling constant $C_Q = eQV_{zz}/h$ and by η .² Hence, the spectrum provides valuable information on the local symmetry around the ^{11}B nucleus.

RESULTS AND DISCUSSION

To investigate the nature of the reaction between boric acid and wood particles in this system, several

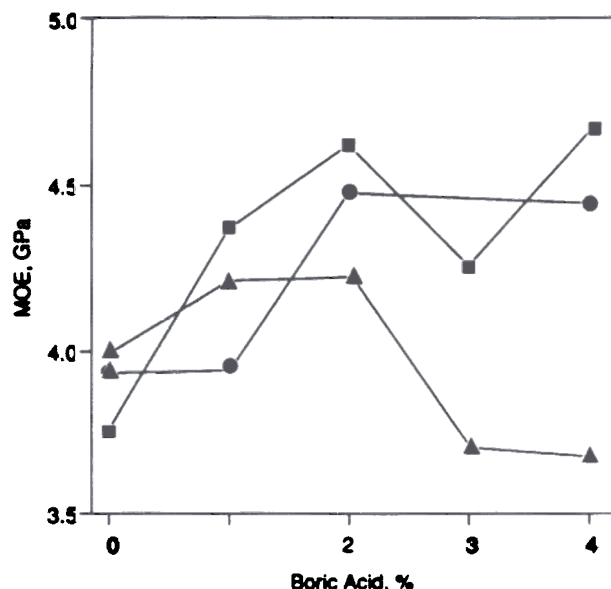


Figure 2 Elastic modulus of 65% polystyrene/35% wood flour as a function of boric acid addition for (●) 3% solvent at 350°F, (■) 0% solvent at 350°F, and (▲) 3% solvent at 380°F.

samples were studied with ^{13}C -CP/MAS NMR. The ^{13}C -NMR spectra are shown in Figures 1–4. Figure 1 depicts the spectra of the starting materials (wood, PS, *m*-pyrol) and their different combinations, without boric acid. The bands given by cellulose and hemicellulose carbons dominate the spectrum of wood³ [Fig. 1(a)]: C1 (105.0 ppm), C4 (88.4 and 83.2 ppm), C2, C3, and C5 (74.6 and 72.3 ppm), and C6 (64.8 and 62.2 ppm). The spectral region corresponding to aromatic carbons of lignin (110–160

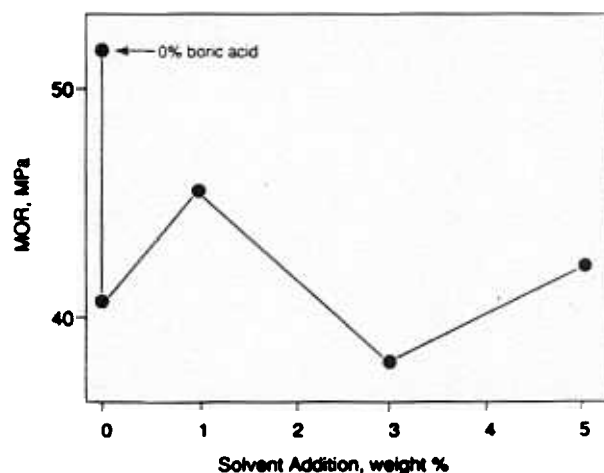


Figure 3 Strength of 65% polystyrene/35% wood flour with 2% boric acid as a function of solvent addition.

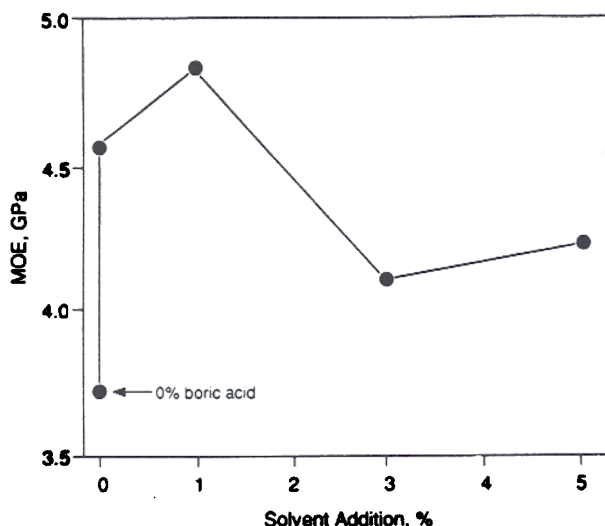


Figure 4 Elastic modulus of 65% polystyrene/35% wood flour with 2% boric acid as a function of solvent addition.

ppm) is not well resolved and the peaks are weak. However, the resonance at 56 ppm, ascribed to the lignin methoxy carbons, is clearly seen.

Figure 1(b) shows the spectrum of PS. The band at 40.5 ppm and the shoulder at ca. 45 ppm are assigned to $-\text{CH}_2-$ and $\text{CH}-$ carbons of the aliphatic backbone of the polymer, respectively. The strong peak at 127.9 ppm is assigned to the tertiary carbons of the aromatic ring, while the band at 146.2 ppm is given by the quaternary carbon of the aromatic ring.²

The spectra corresponding to the wood/PS melt, with and without *m*-pyrrol [Fig. 1(d) and (c), respectively], do not present significant changes compared to the spectra of wood and PS alone. This indicates that no chemical interaction takes place between the two polymer systems.

The spectrum of wood (without PS) treated with boric acid [Fig. 2(b)] shows a slight broadening of the bands assigned to C6 (64.8 and 62.2 ppm) and the bands assigned to C3, C5, and C6 (74.6 and 72.3 ppm), when compared to the spectrum of untreated wood [Fig. 2(a)]. This could be an indication of a change of the chemical environment surrounding these carbon atoms, with the treatment of wood with boric acid. The spectrum of PS (without wood) treated with boric acid [Fig. 3(b)] is not significantly different from the spectrum of nontreated PS alone [Fig. 3(a)], indicating that no chemical interaction has occurred between boric acid and PS. The results obtained for wood and PS alone, treated with boric acid, are not easily visible in the spectra

of wood/PS materials treated with boric acid [Fig. 4(c) and (d)] since these spectra are dominated by the peaks assigned to PS.

¹¹B-MAS NMR

The ¹¹B-MAS NMR spectra are shown in Figure 5. The HPDEC spectrum of boric acid (see inset) displays a second-order quadrupole powder pattern characteristic of boron in trigonal environment. The MAS spectrum of boric acid [Fig. 5(a)] still shows the quadrupole doublet, although the line is broadened by dipolar coupling with B—OH protons. The spectra of boric acid samples treated at 350 and 380°F (not shown) are similar to the room temperature spectrum [Fig. 5(a)]. The spectrum given by PS treated with boric acid [Fig. 5(b)] shows that boron remains in trigonal coordination, hence providing no evidence for chemical bonding. The spectra of wood + boric acid [Fig. 5(c)] and wood + PS

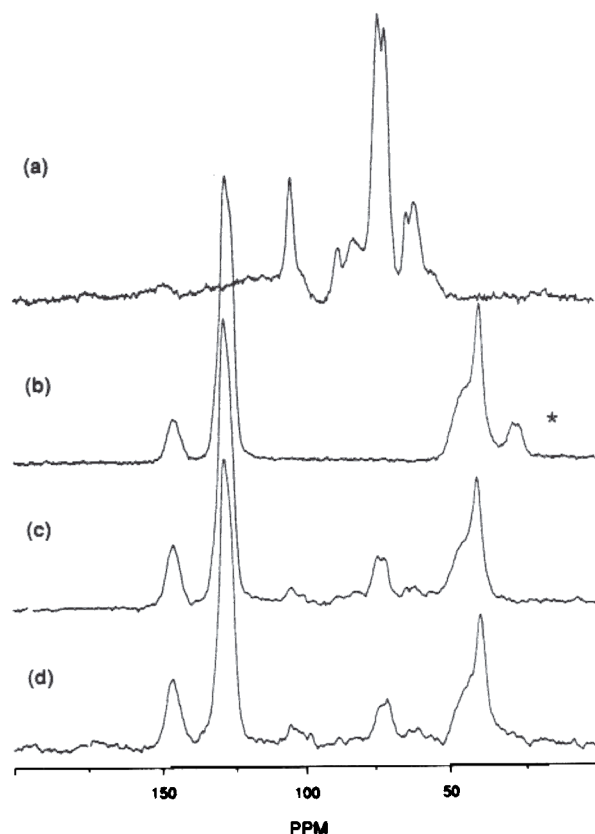


Figure 5 ¹³C-CP/MAS NMR spectra of (a) wood (10 kHz), (b) PS (10 kHz), (c) 65/35 PS/wood flour, 0% boric acid, and 0% solvent (15 kHz), and (d) 65/35 PS/wood flour, 0% boric acid, and 3% solvent (15 kHz). The asterisk denotes spinning side bands.

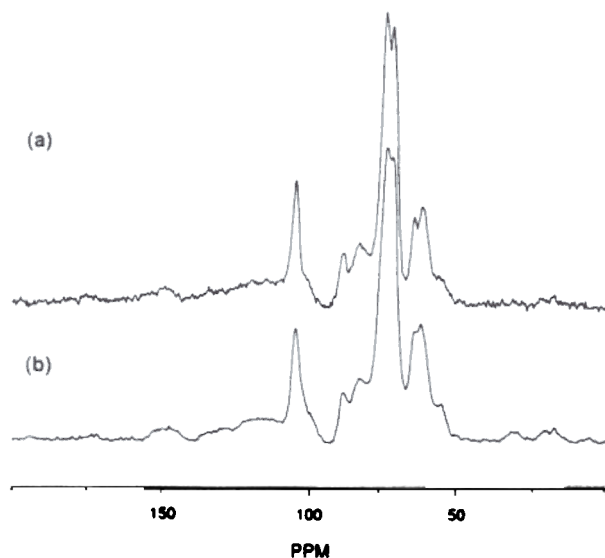


Figure 6 ^{13}C -CP/MAS NMR spectra of (a) wood flour (10 kHz) and (b) wood flour, 4% boric acid, and 3% solvent (15 kHz).

+ boric acid [Fig. 5(d)] contain both a second-order quadrupole powder pattern due to trigonal boron and a sharp signal at ca. -1 ppm, characteristic of boron in tetrahedral coordination. The latter resonance indicates that the coordination of some boron atoms has changed from trigonal to tetrahedral and, therefore, suggests that boron bonds to wood. Although the coordination of boron to lignin cannot be excluded,⁴ the coordination of boron to wood

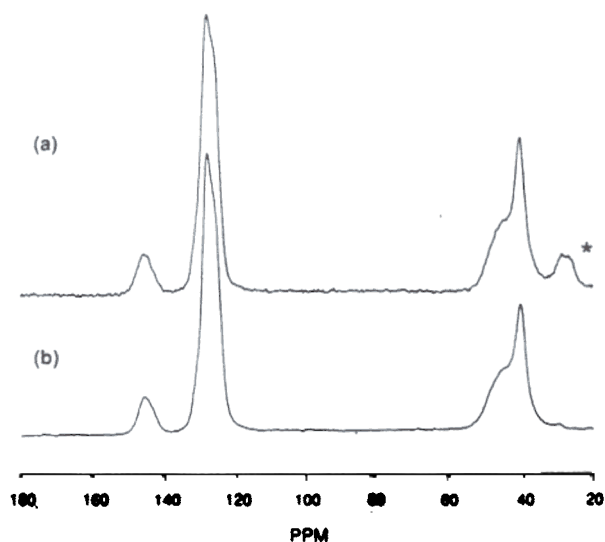


Figure 7 ^{13}C -CP/MAS NMR spectra of (a) PS (10 kHz) and (b) PS, 4% boric acid, and 3% solvent (13.5 kHz). The asterisk denotes spinning side bands.

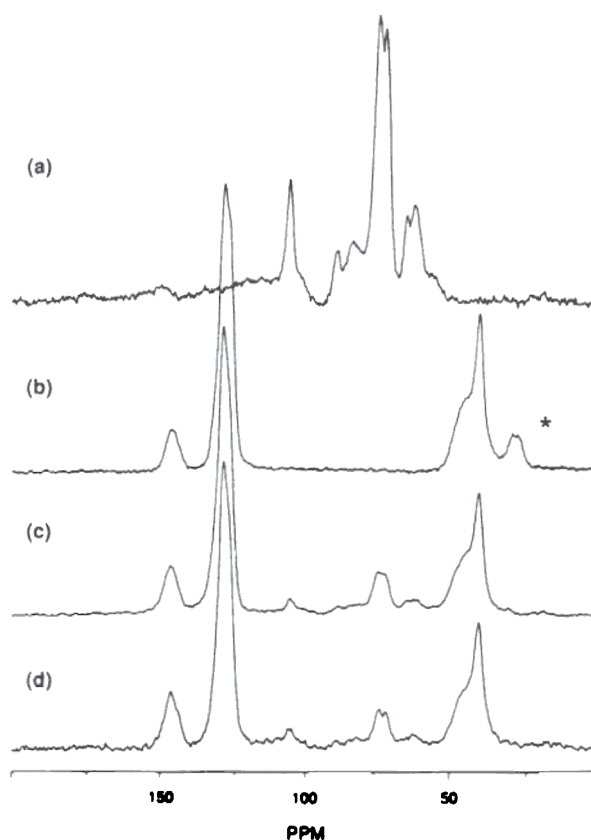


Figure 8 ^{13}C -CP/MAS NMR spectra of (a) wood (10 kHz), (b) PS (10 kHz), (c) 65/35 PS/wood flour, 4% boric acid, and 3% solvent at 350°F (15 kHz), and (d) 65/35 PS/wood flour, 4% boric acid, and 3% solvent at 380°F (15 kHz). The asterisk denotes spinning side bands.

polysaccharides is more likely to occur as suggested by extensive solution studies of the coordination of boron to carbohydrates in tetrahedral arrangements⁵ (Fig. 6, structures II, III, and IV). However, we cannot exclude the possibility that some trigonal boron might be coordinated to wood polysaccharides⁵ (Fig. 6, structure I). Such a site would probably give a second-order quadrupole powder pattern with an isotropic chemical shift and quadrupole parameters slightly different from those of boric acid. It is clear from Figure 5 that the shape of the quadrupole doublet changes from sample to sample. This would support the presence of such trigonal environments. However, since the NMR spectra were recorded with an echo pulse sequence which may introduce distortions in the line shapes, we stress that this remains a speculation and that this area needs much work.

Mechanical properties testing indicated that the strength of the composite was reduced by the pres-

ence of boric acid (Fig. 7). While the presence of 3% *m*-pyrol slightly elevated the MOR over that of no plasticizer, mixing the components at 380°F clearly reduced composite strength.

The stiffness was markedly improved with boric acid concentrations up to 2% (Fig. 8). The improvement in stiffness was less pronounced for the samples blended at 380°F. At the higher boric acid concentrations of 3 and 4%, the stiffness of the 380°F samples decreased. This may be a result of reaction between the boric acid and the wood fibers, assuming that the reaction rate is dependent upon boric acid concentration and temperature. The differences in stiffness between samples with and without *m*-pyrol as the plasticizer were insignificant.

The influence of *m*-pyrol on strength was insignificant up to 5% additions (Fig. 9). Stiffness showed a slight improvement at 1% addition, but further additions reduced the overall stiffness (Fig. 10). The effect of *m*-pyrol was not as great as was the effect

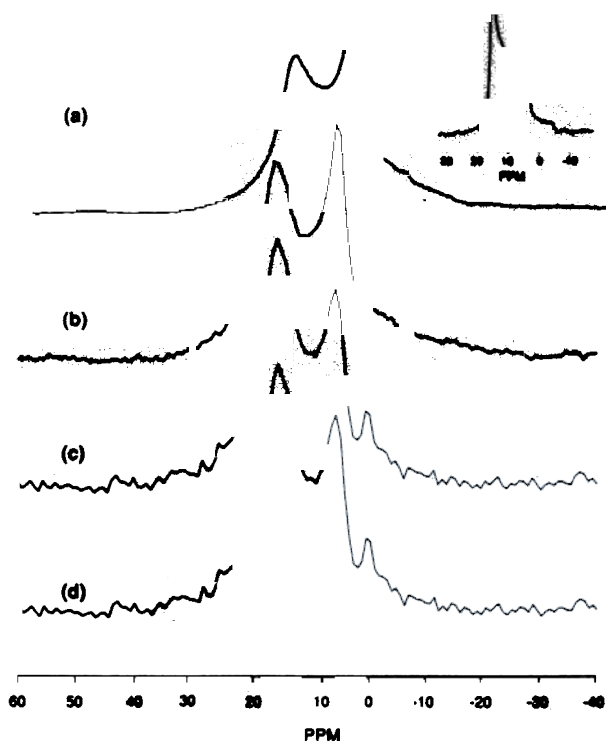


Figure 9 ^{11}B -MAS NMR spectra of (a) boric acid, (b) PS, 4% boric acid, and 3% solvent (15 kHz), (c) wood flour, 4% boric acid, and 3% solvent (15 kHz), and (d) 65/35 PS/wood flour, 4% boric acid, and 3% solvent (spinning rates: 13–15 kHz). The inset depicts the spectrum of boric acid recorded with a Bolch decay and high-power proton decoupling.

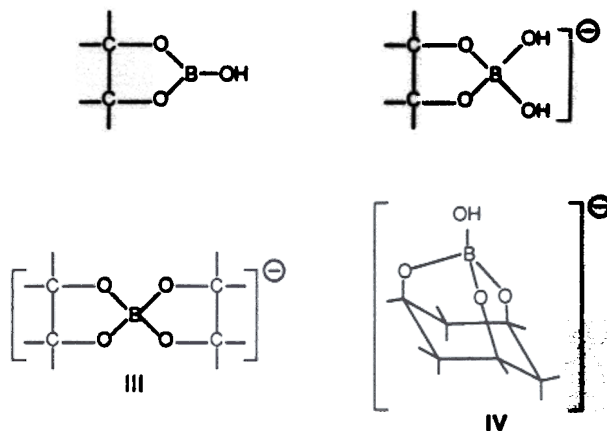


Figure 10 Potential structures of complexes between boric acid/borates and carbohydrates.⁵

of boric acid on composite mechanical properties. Addition of 2% boric acid improved the stiffness with only about a 5% reduction in strength (Figs. 9 and 10).

The reaction between boric acid and wood was further elucidated by extracting the formed composite and analyzing the extractants. After removing the PS by toluene extraction, the remaining fiber was extracted with boiling water. The boric acid content of the water solution was determined by X-ray fluorescence spectroscopy. The solution contained 89.5% of the original boric acid. This extreme condition should have removed any unreacted boric acid. It may also have saponified some of the borate esters and therefore may be underreporting the actual content of the boric acid reacted with wood particles. The wood remaining after extraction was digested and the resulting solution analyzed for boric acid via ICP. The analysis showed that the boiling water-extracted wood particles still contained 2.1 g/kg as boric acid compared to a blank sample run under the same conditions. These data support the NMR results, suggesting that, while the extent of reaction was not large, some of the boric acid reacted chemically with the wood filler.

Additional evidence was observed optically. The samples which contained boric acid showed a red coloration under microscopic examination. A color change can be indicative of a chemical reaction.

The glass transition temperature (T_g) of the PS was lowered 2.0°C, from 105.2 to 103.2°C, by the addition of wood flour to the system (Fig. 11). The addition of 3% plasticizer resulted in a large drop in the T_g from 103.2 to 96.1°C. Boric acid addition had only a small effect on the T_g , lowering it from 96.1 to 95.5°C. These data support our hypothesis

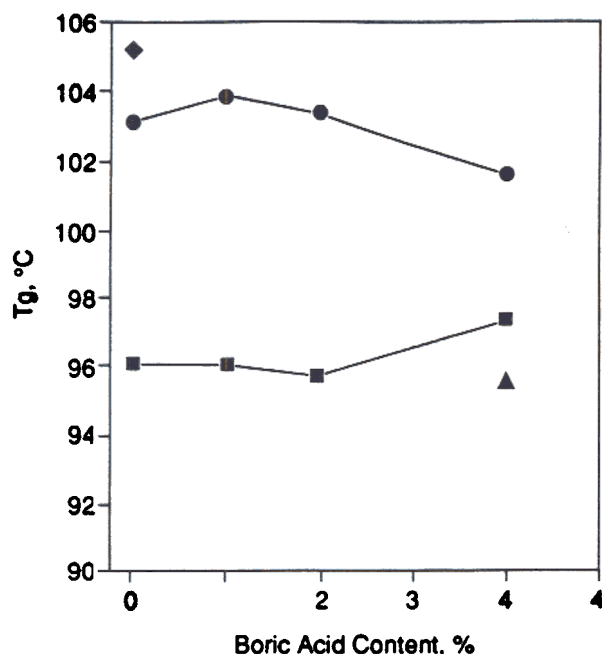


Figure 11 Glass transition temperatures from DSC measurements for (♦) PS, no wood, no additives, (●) 65/35 PS/wood flour, no solvent, (■) 65/35 PS/wood flour, 3% solvent, and (▲) PS, no wood, 3% solvent.

that PS does not react with boric acid under these conditions. The decrease in the PS T_g with plasticizer addition was expected. The small change in T_g upon boric acid addition also indicates that while there appears to be reaction between the wood and the boric acid it does not translate into changes in the interaction between the wood and the PS that would affect the T_g .

This hypothesis is supported by the DMA data presented in Fig. 12. Figure 12(a) indicates that the addition of 6% plasticizer lowers the T_g , obtained from $\tan \delta$, approximately 13°C, from 115 to 102°C. Addition of 1% boric acid lowers the T_g an additional 4° to approximately 98°C. At 4% boric acid, the T_g is once again 102°C. The cause of this rise in T_g with boric acid addition is unknown. The samples containing the plasticizer also exhibit a shoulder at approximately 80–90°C. This feature of the $\tan \delta$ spectra was observed in earlier work.⁶ It may indicate some sort of interaction between the wood and PS phases. This interaction may be of the form of an additional or altered interphase between the PS and the wood surface. If the plasticizer were preferentially located close to the wood surface, the PS associated with that region might conceivably present a lowered T_g , thus accounting for the low-temperature shoulder. This speculation cannot be con-

firmed or denied without additional study. In Figure 12(b), the E' curves show that the presence of the plasticizer reduces the E' value at equivalent temperatures. The addition of 1% boric acid appears to increase the E' value at low temperatures, but lowers the onset temperature of the phase transition.

The increase in stiffness and E' of the composites might be accounted for if the boric acid is embrittling the wood flour. The temperature of the blending operation (350°F) is certainly high enough to dehydrate the wood. Heat treatment is

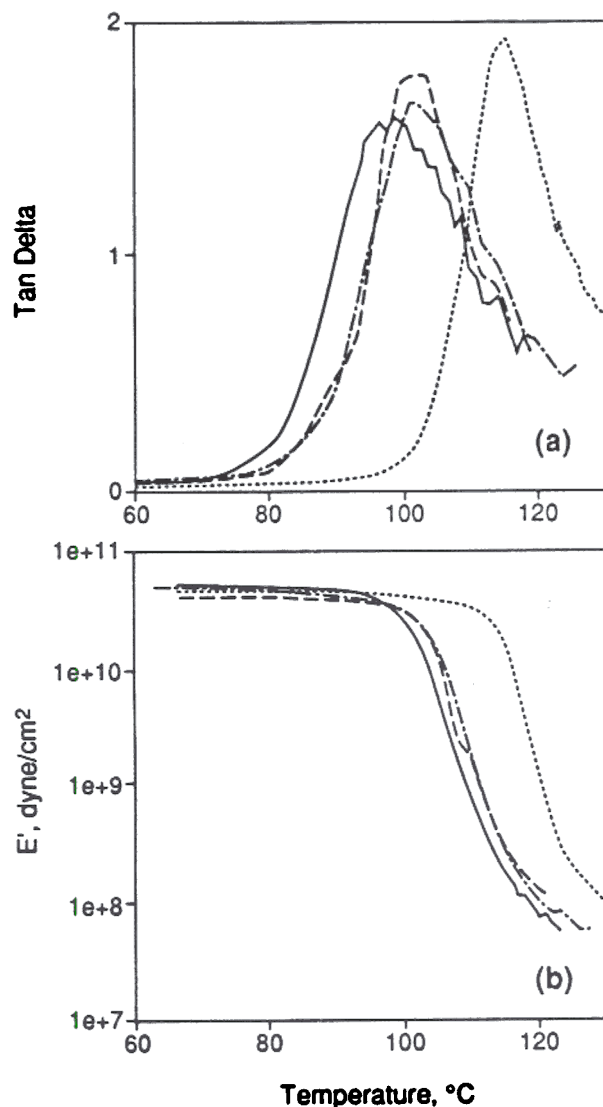


Figure 12 DMA of samples with (· · · · ·) 0% solvent and 0% boric acid, (— · —) 6% solvent and 0% boric acid, (— · —) 6% solvent and 1% boric acid, and (—) 6% solvent and 4% boric acid. (a) $\tan \delta$; (b) E' .

known to dimensionally stabilize and simultaneously embrittle wood.^{7,8} If the high temperatures and acidic environment experienced by the wood in these experiments embrittled the wood, it might explain the increase in stiffness. Also, if embrittlement is the only reaction facilitated by boric acid addition, we would expect no increase in ultimate strength and little change in the T_g and DMA spectra, which is consistent with the data. Clearly, these limited data do not allow firm conclusions regarding wood embrittlement. Much more work is needed in this area.

CONCLUSIONS

Solid-state NMR has been shown to be a powerful technique to study the interaction of boron with the polymer constituents of a wood/polystyrene composite material. ¹¹B-MAS NMR and ¹³C-CP/MAS NMR evidence suggest that boron chemically bonds to wood components during the preparation of a composite material of wood + PS + boric acid. The formation of tetrahedral complexes of boron and (probably) wood polysaccharides has been put in evidence. However, the formation of trigonal complexes between boron and wood components cannot be excluded. No evidence has been found for chemical interaction between boron and PS.

The stiffness of wood-PS composites was increased for certain addition levels of boric acid. The strength was marginally decreased by boric acid addition under certain conditions. This may be due to embrittlement of the wood phase at the high temperatures of the experiments, accelerated by the reaction of boric acid. The slight changes in ultimate properties and DMA spectra suggest that the interphasal properties of the composites are little changed by the reaction of boric acid with wood. The T_g of PS decreased substantially with the addition of the plasticizer to the wood/PS system, as expected. The

plasticizer seemed to have little effect on composite properties or the boric acid-wood reaction other than plasticization.

While these studies do not reveal large improvements in the properties of the composite under investigation, they do illustrate the potential for reactive extrusion in the development of advanced wood-polymer composites. Chemical reactions may be performed on the wood substrate in the molten polymer matrix without significant alteration of the properties of the matrix. Hopefully, these results support the development of new techniques to improve the material properties of wood-polymer composites.

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